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REE potential of organic-rich shales

A preliminary assessment

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Rare earth elements (REE)

IA																												VII							
1	H																					2	He												
II																		III		IV		V		VI		VII									
3	Li	4	Be																	5	B	6	C	7	N	8	O	9	F	10	Ne				
11	Na	12	Mg																	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar				
		III		IV		V		VI		VII		VIII		I		II																			
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba	57	La	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
87	Fr	88	Ra	89	Ac	104	Rf	105	Db	106	Sg	107	Bh	108	Hs	109	Mt																		

* Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Critical
 Near-critical
 Non-critical

39
Y
 Note: Pm has no natural occurrence

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
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Light REE

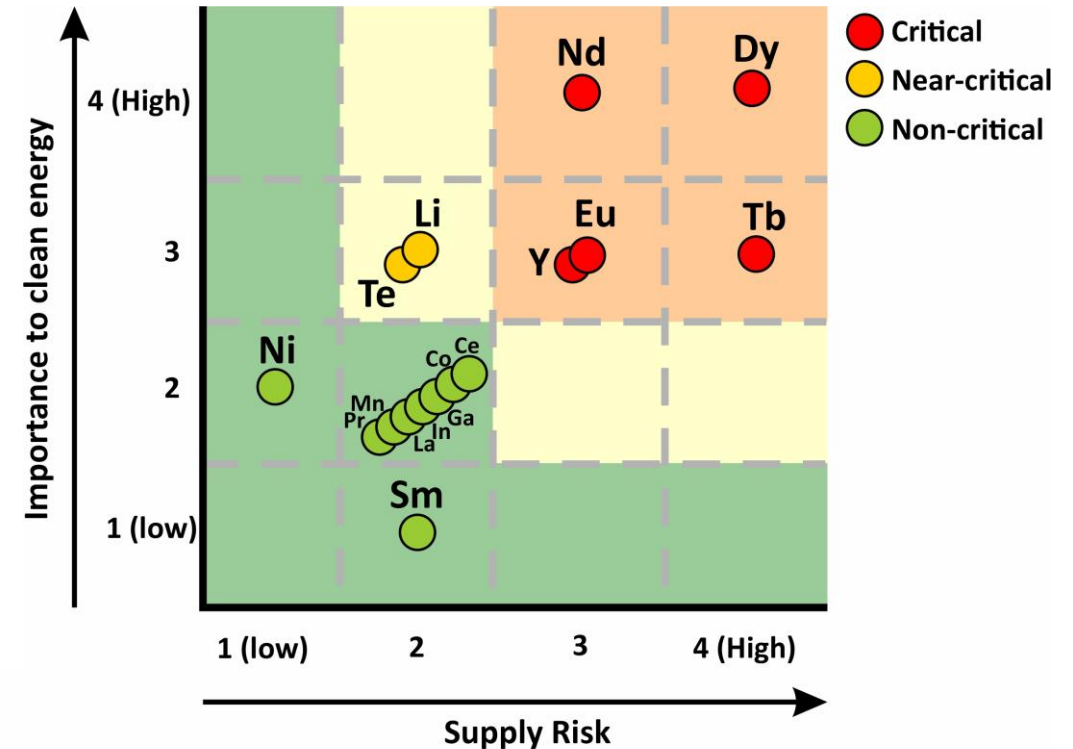
Heavy REE

Light REY

Medium REE
(Includes Y)

Heavy REY

Rare earth elements (REEs) include the 15 lanthanides from lanthanum (La) to lutetium (Lu) with atomic numbers of 57–71, accompanied by chemically similar yttrium (Y).



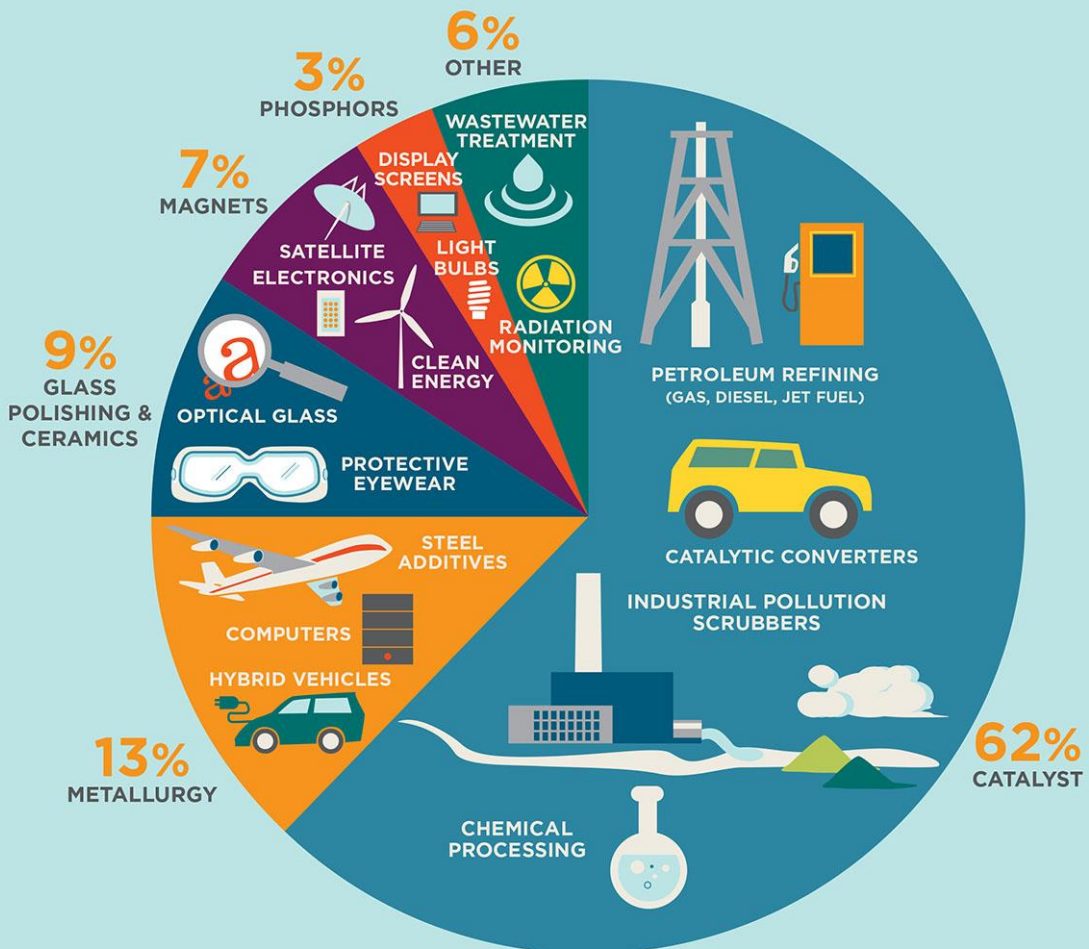
Nd: Neodymium; Dy: Dysprosium; Eu: Europium; Y: Yttrium; Tb: Terbium; Li: Lithium; Te: Tellurium;
 Ni: Nickel; Ce: Cerium; Co: Cobalt; Ga: Gallium; In: Indium; La: Lanthanum; Mn: Manganese;
 Pr: Praseodymium; Sm: Samarium

U.S. Department of Energy, 2011

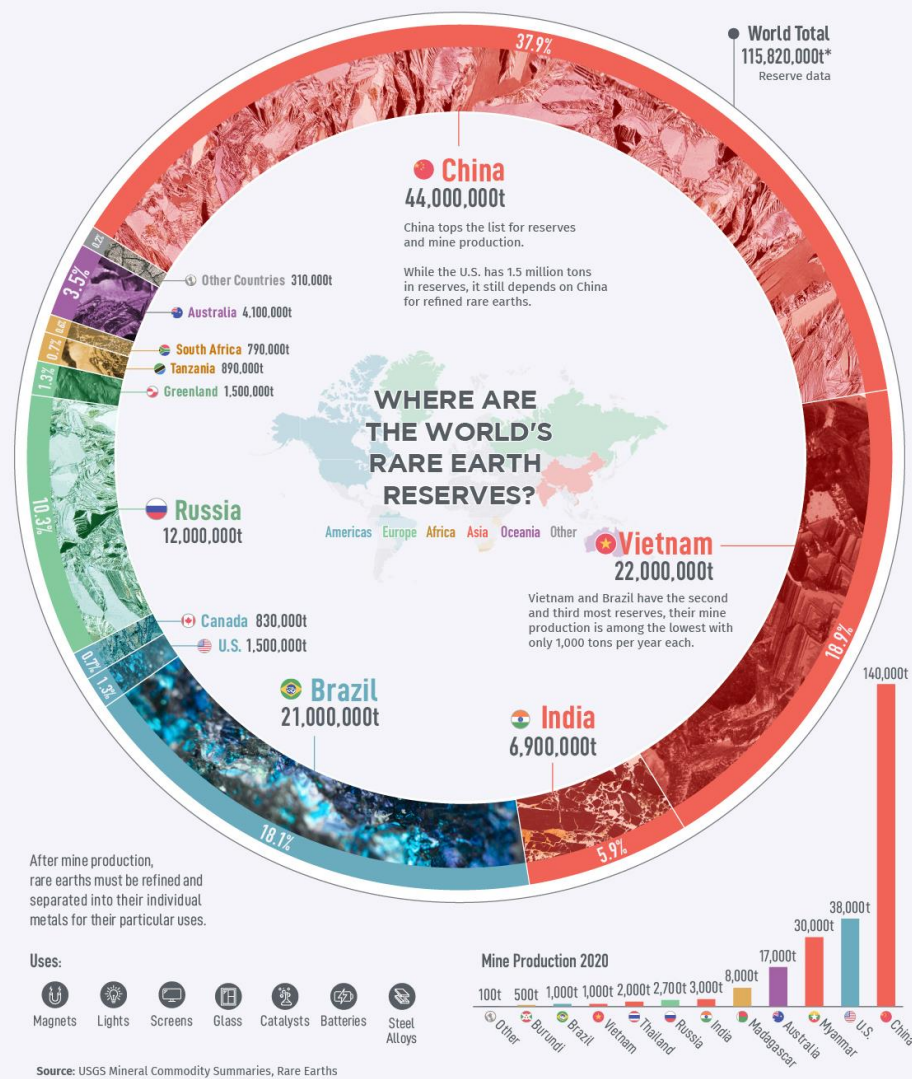


REEs use and resources

US Rare Earths Usage



DATA SOURCE: UNITED STATES GEOLOGICAL SURVEY (2013)



<https://elements.visualcapitalist.com>



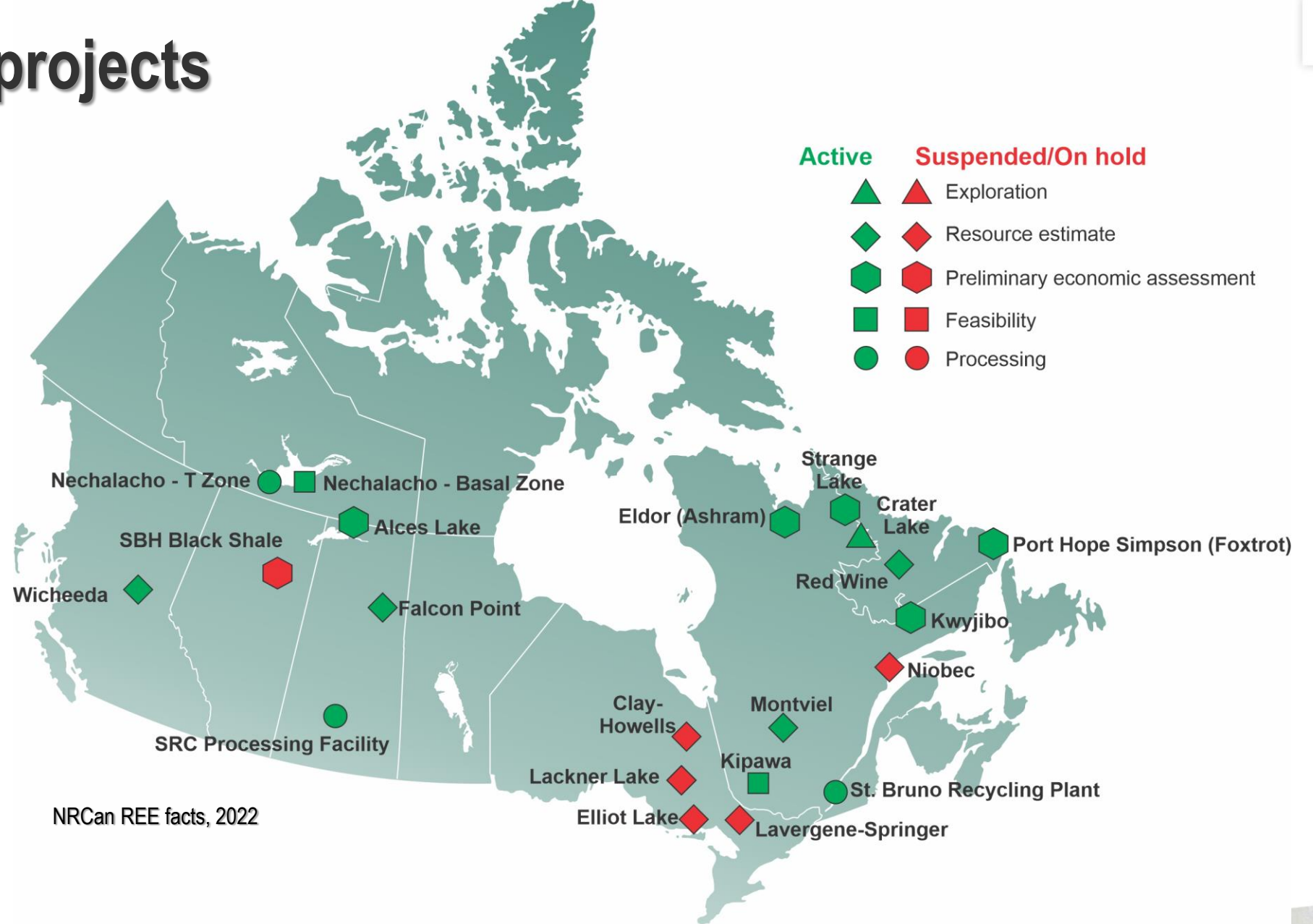
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Canadian REE projects

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Canadian REE projects

Bloomberg

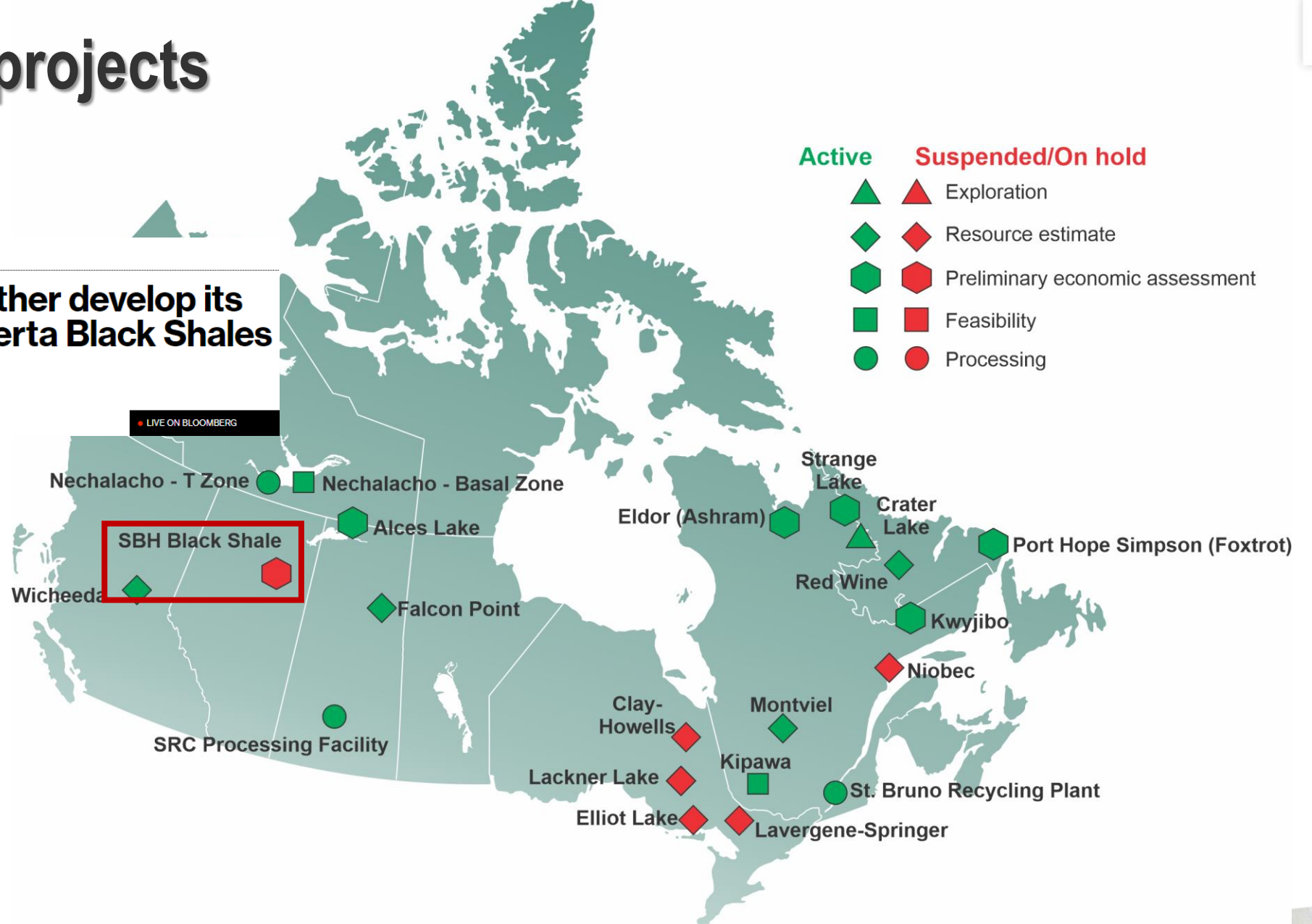
DNI Metals - Signs LOI to further develop its Vanadium / Polymetallic Alberta Black Shales deposit

December 18, 2018, 5:39 AM MST

Buckton - Polymetallic Deposit - Alberta Canada



<https://www.dnimetals.com/projects-2>

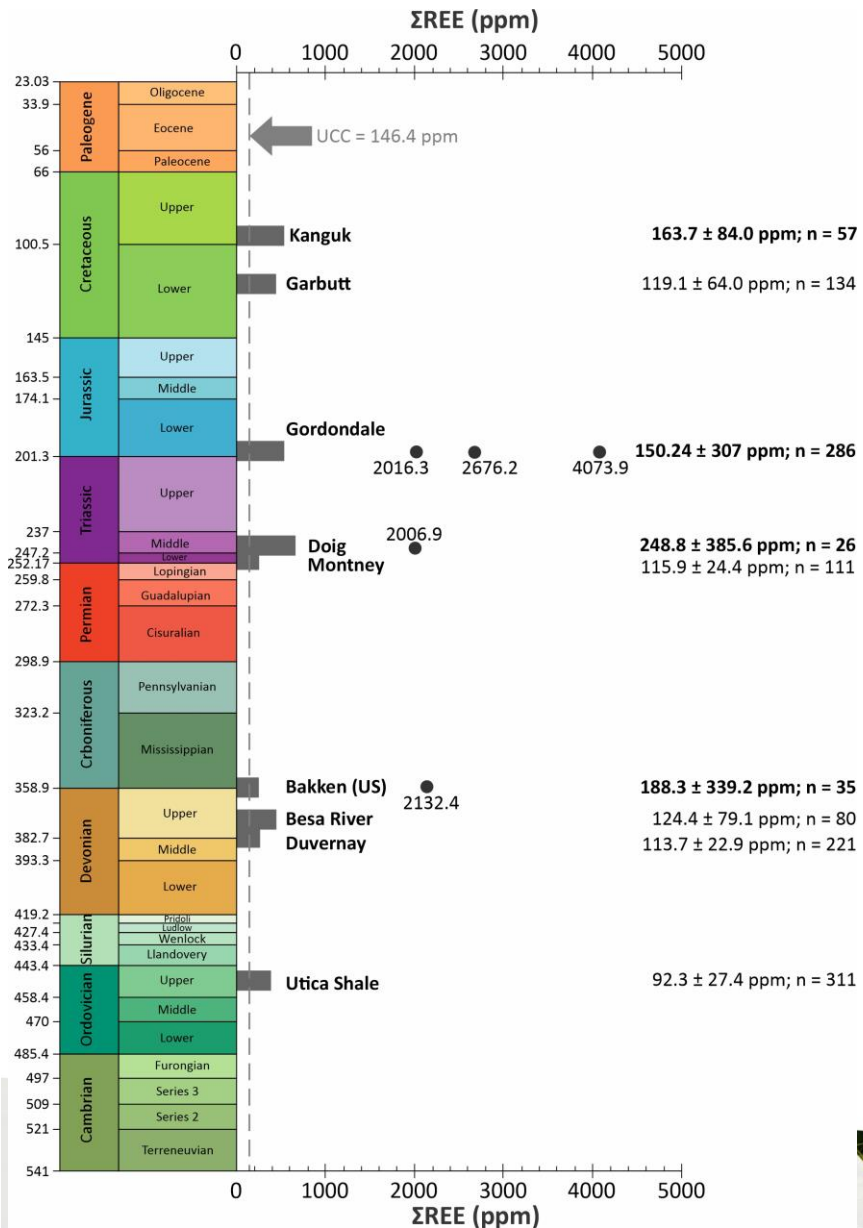


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Canadian Phanerozoic black shales REE content



GEOLOGICAL SURVEY OF CANADA
OPEN FILE XXXX

Rare Earth Element (REE) content of shale, coal and coal byproducts, and potential for Canadian REE supply – A literature review and initial assessment

O.H. Ardakani, K. Biggart, K. Dewing

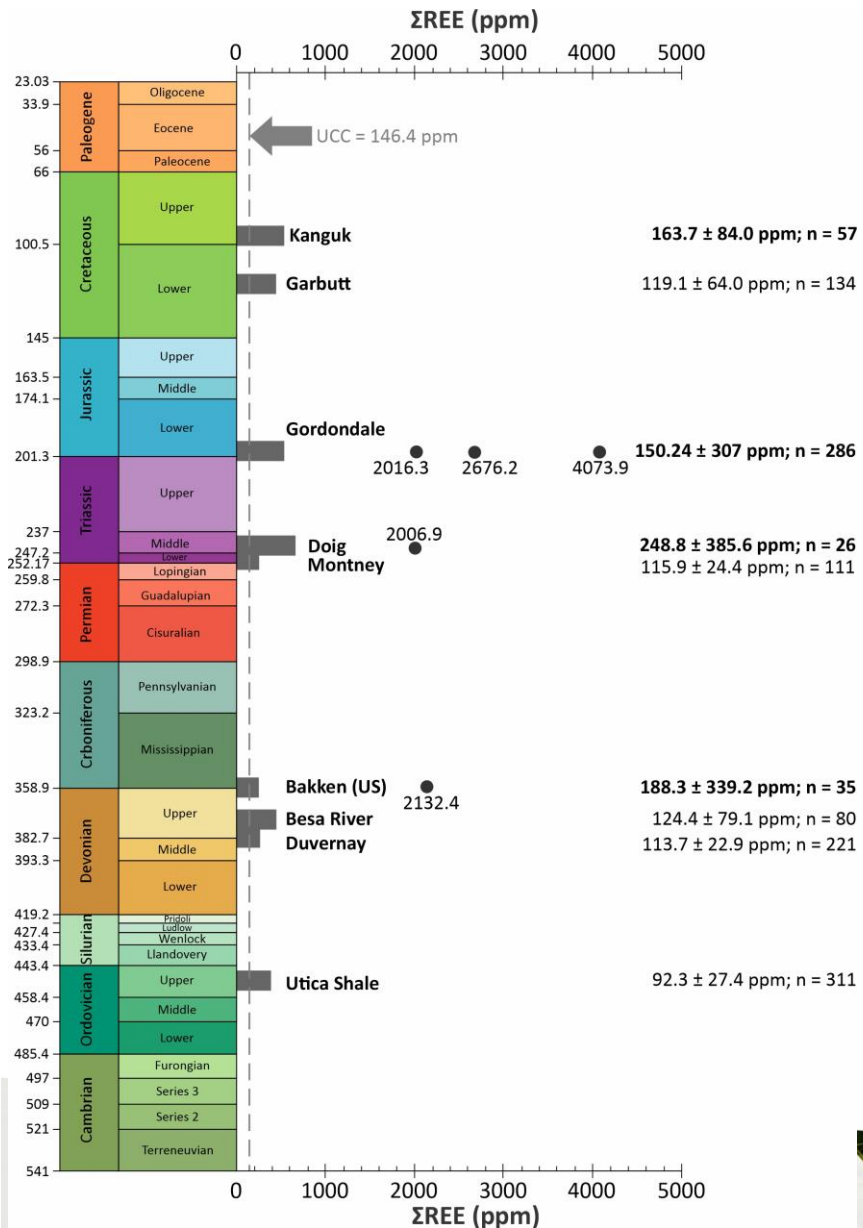
2022



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Canadian Phanerozoic black shales REE content

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2022

Ore Geology Reviews 107 (2019) 600–614



Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev



GEOLOGICAL SURVEY OF CANADA
OPEN FILE XXXX

Rare Earth Elements of Permian through Cretaceous strata of the Sverdrup Basin

S.E. Grasby and J. Galloway

2021

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THE GEOLOGICAL SOCIETY OF AMERICA®

<https://doi.org/10.1130/G46874.1>

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A Middle Devonian basin-scale precious metal enrichment event across northern Yukon (Canada)

M.G. Gadd¹, J.M. Peter¹, D. Hnatyshin², R. Creaser², S. Gouwy³ and T. Fraser⁴

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²Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2R3, Canada

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Platinum, Pd, Mo, Au and Re deportment in hyper-enriched black shale Ni-Zn-Mo-PGE mineralization, Peel River, Yukon, Canada

Michael G. Gadd*, Jan M. Peter, Simon E. Jackson, Zhaoping Yang, Duane Petts

Geological Survey of Canada, 601 Booth St., Ottawa, Ontario K1A 0E8, Canada



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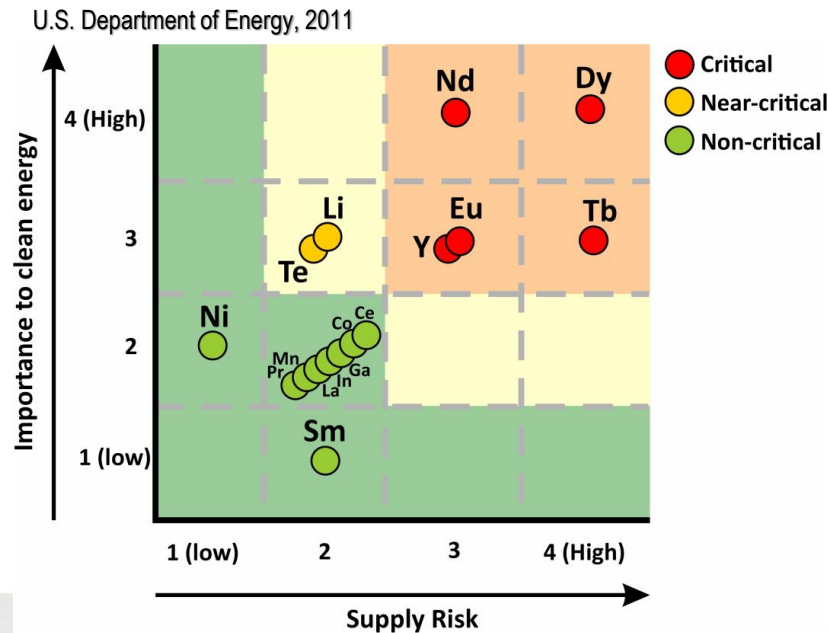
Classification of shales - outlook for REY composition

REY are divided into **critical** (Nd, Eu, Tb, Dy, Er, and Y), **uncritical** (La, Pr, Sm, and Gd) and **excessive** (Ce, Ho, Tm, Yb, and Lu) groups.

$$C_{outl} = \frac{\frac{(Nd + Eu + Tb + Dy + Er + Y)}{\Sigma REY}}{\frac{(Ce + Ho + Tm + Yb + Lu)}{\Sigma REY}}$$

$$\%REY = \frac{(Nd + Eu + Tb + Dy + Er + Y)}{\Sigma REY}$$

Seredin & Dai (2012) International Journal of Coal Geology 94 67–93



Nd: Neodymium; Dy: Dysprosium; Eu: Europium; Y: Yttrium; Tb: Terbium; Li: Lithium; Te: Tellurium;
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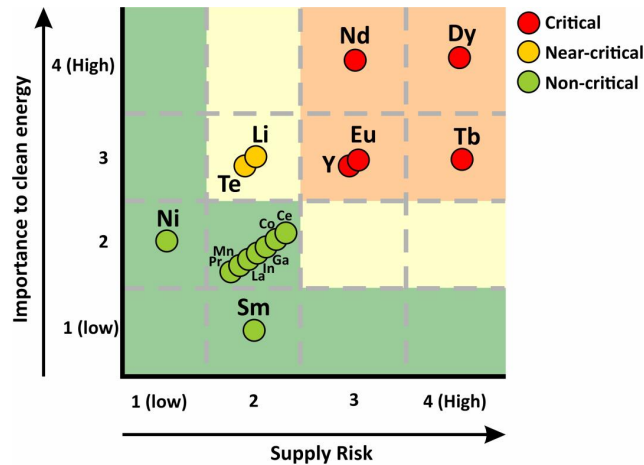
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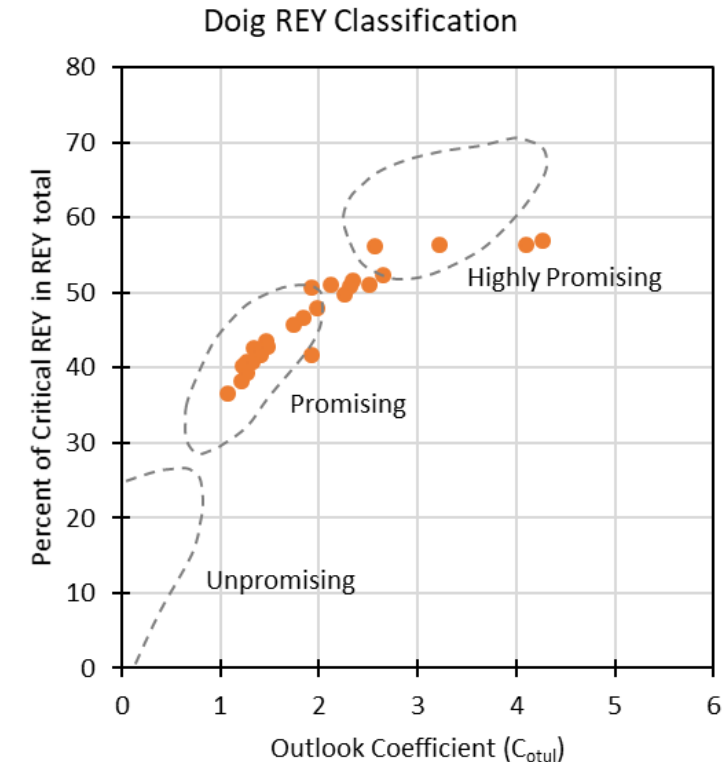
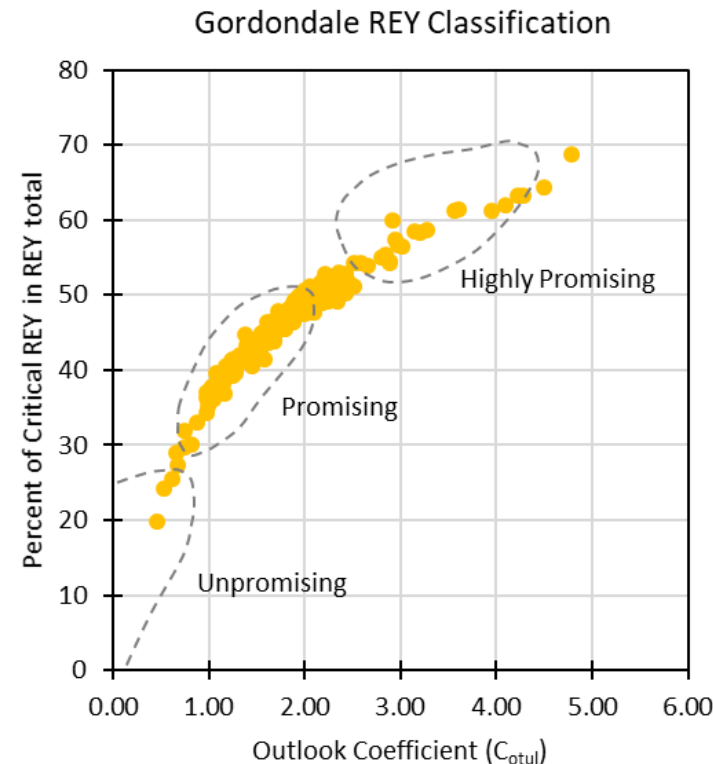
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U.S. Department of Energy, 2011

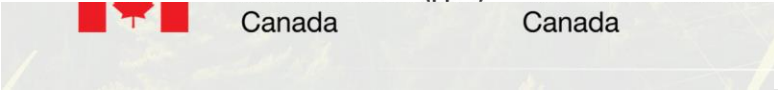
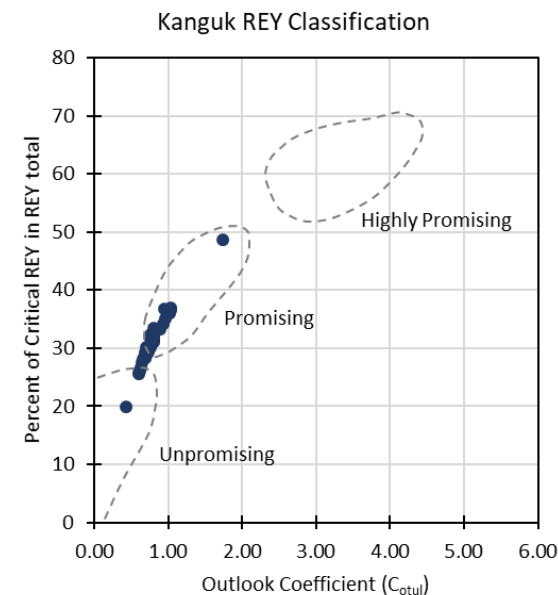
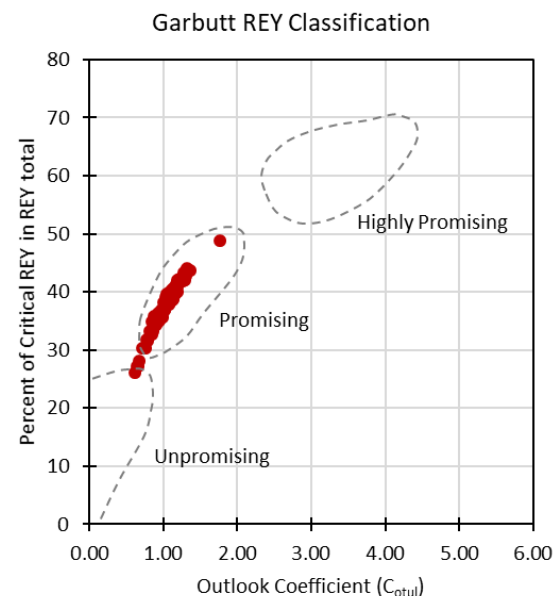
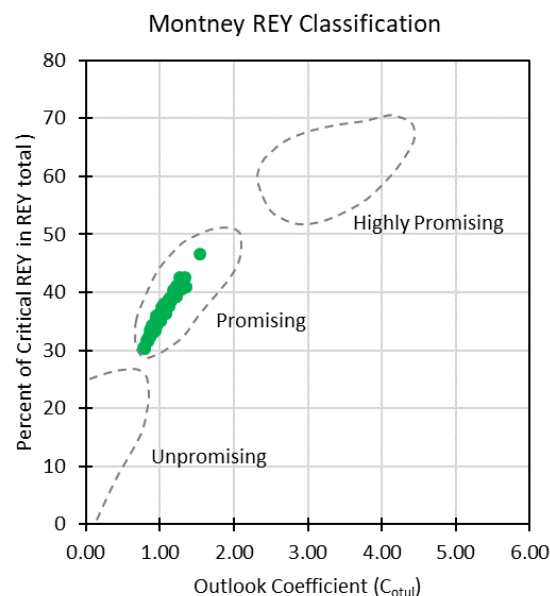
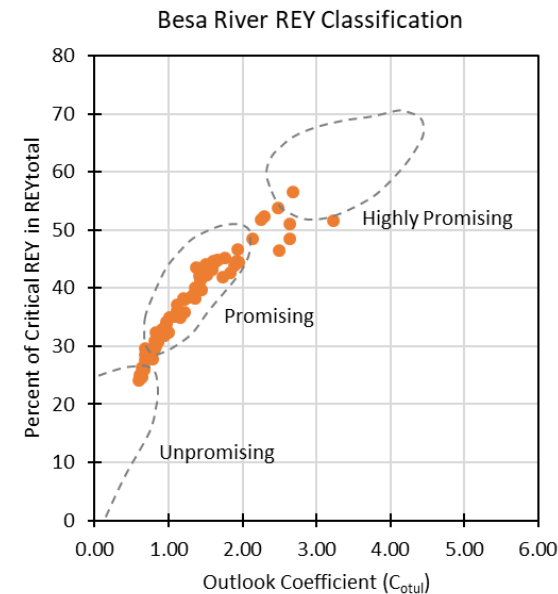
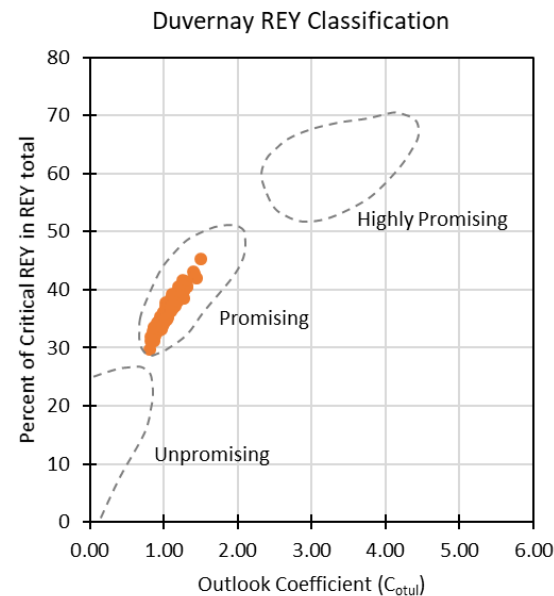
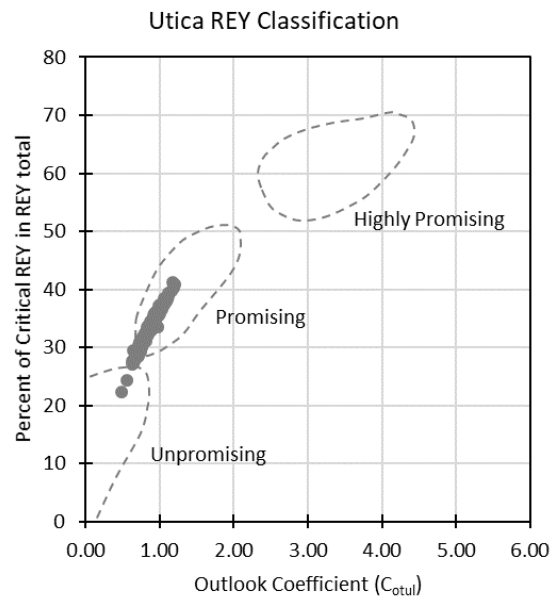
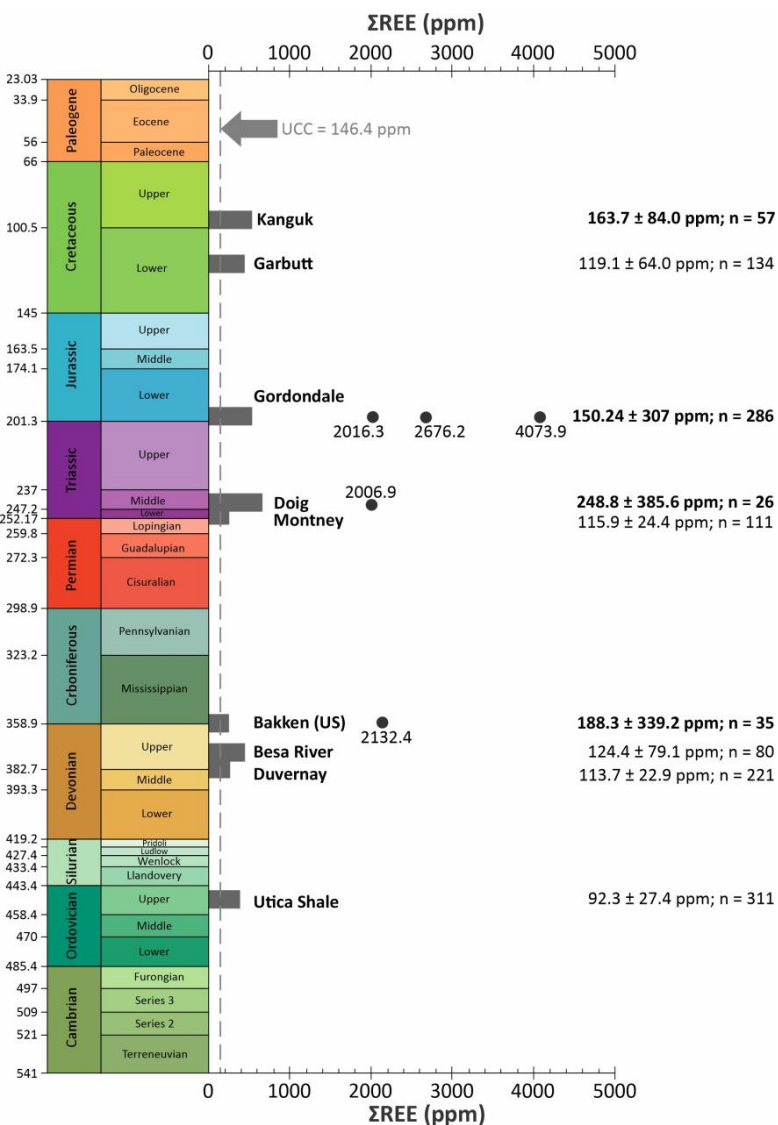


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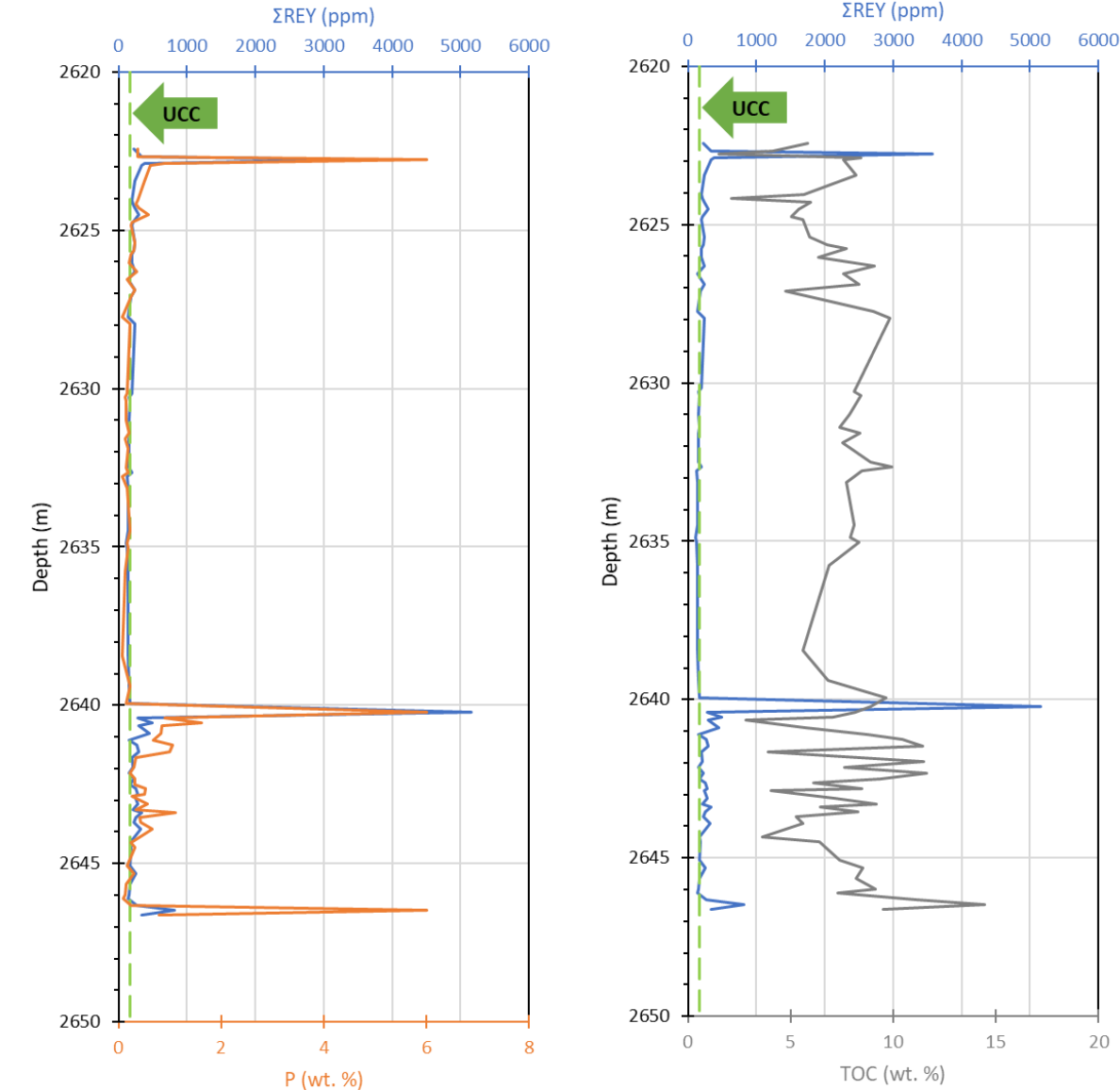
Classification of shales



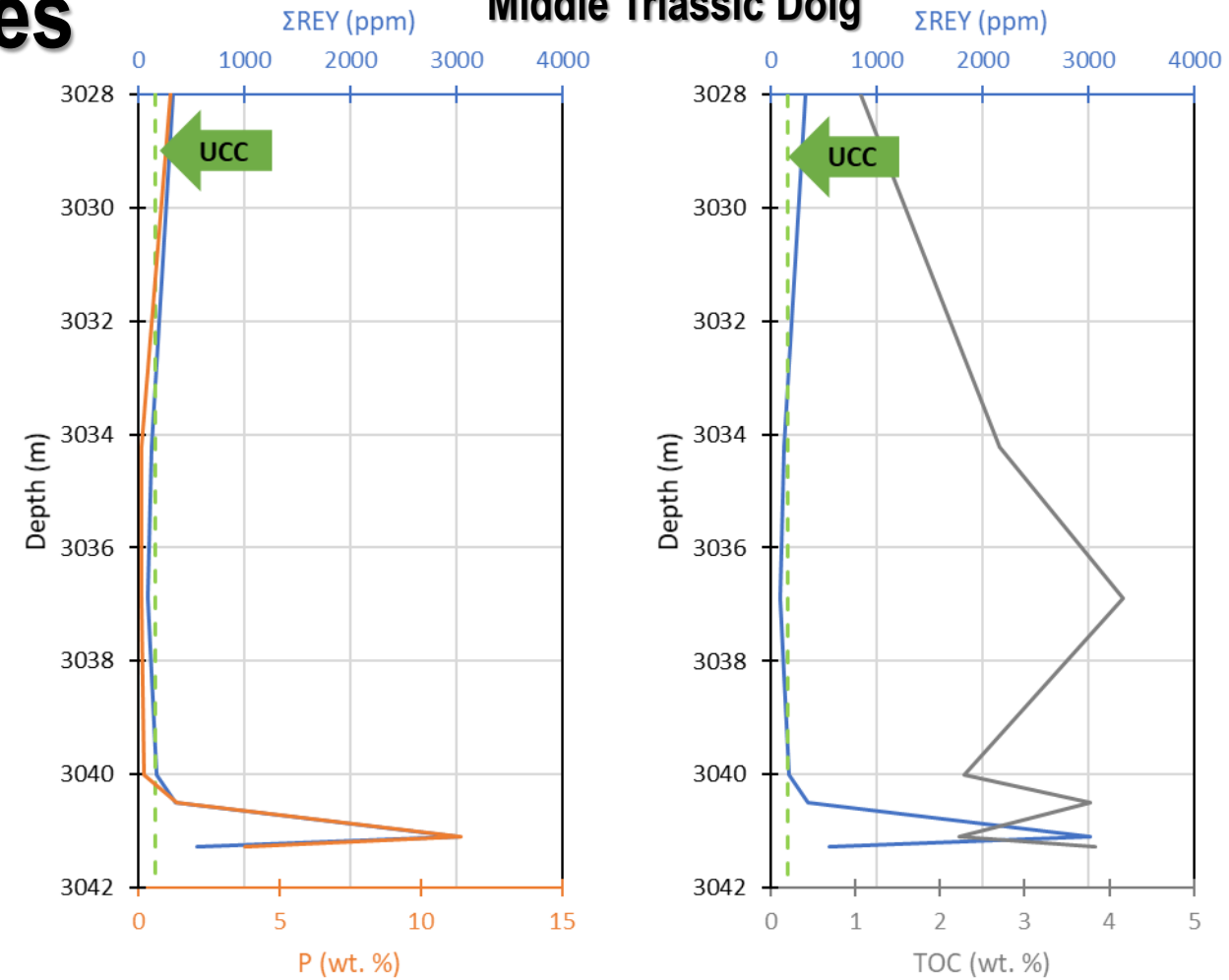
REY content of phosphatic shales

UCC Σ REY = 168.4 ppm

Early Jurassic Gordondale



Middle Triassic Doig



GR focus review

Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis?

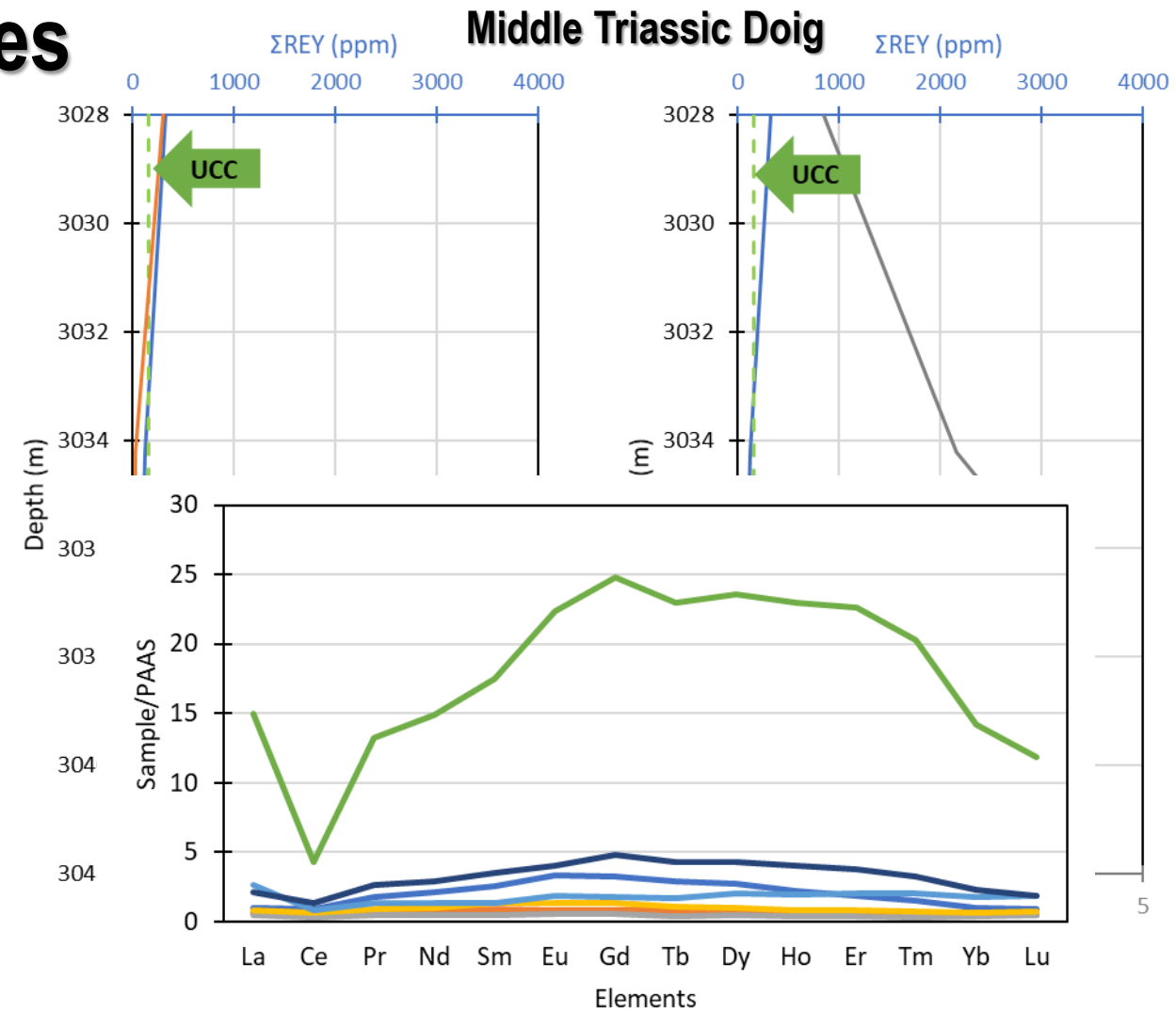
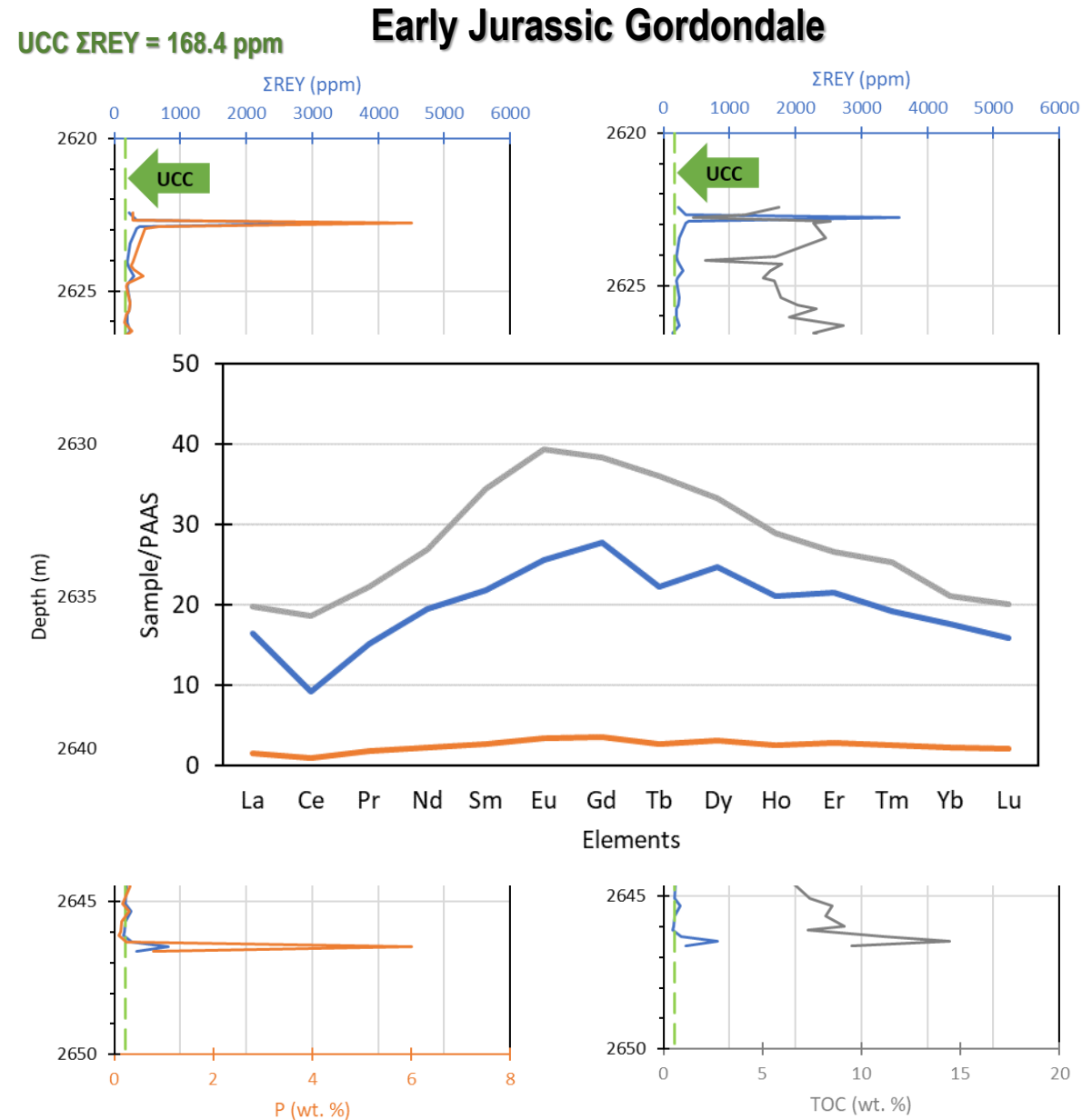
Poul Emsbo^{a,*}, Patrick I. McLaughlin^b, George N. Breit^a, Edward A. du Bray^a, Alan E. Koenig^a

^a U.S. Geological Survey, Box 25046, MS-973, Denver Federal Center, Denver, CO 80225, USA



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REY content of phosphatic shales



Sequential extraction scheme used for speciation of metals

The sample was sequentially leached in three steps following the modified BCR (European Communities Bureau of Reference) extraction scheme used for operational speciation of metals.

Davranche et al. (2011) Chemical Geology 284 127–137

Step	Soil phases	Extractant	Shaking time and temperature
F1	Water- and acid-soluble and exchangeable	40 mL 0.11 M CH ₃ COOH	16 h at room temperature
F2	Reducible	40 mL 0.5 M NH ₂ OH.HCl (pH 2)	16 h at room temperature
F3	Oxidizable	10 mL 8.8 M H ₂ O ₂ (pH 2)	1 h at room temperature
		10 mL 8.8 M H ₂ O ₂ (pH 2)	1 h at 85 °C
		50 mL 1 M NH ₄ Oac (pH 2)	16 h at room temperature
F4	Residual	15 mL aqua regia	Heating to dryness
		10 mL aqua regia	

Bai et al. (2011) J Fuel Chem Technol, 39 (7) 489-494

Process	Fraction	Extraction solution	Operation condition
I	Exchangeable fraction	MgCl ₂ (1 mol/L pH=7)	Shake for 4 h at room temperature
II	Carbonate bound fraction	CH ₃ COONa (1 mol/L pH=5)	Shake for 5 h at room temperature
III	Ferromanganese oxyhydroxides bound fraction	CH ₃ COOH (25% 0.04 mol/L HONH ₃ Cl)	Shake for 5 h at 90°C
IV	Sulfide bound fraction	HNO ₃ (2 mol/L)	Shake for 6 h at 90°C
V	Organic matter bound fraction	HNO ₃ (0.02 mol/L)+H ₂ O ₂ (30%)	Shake for 2 h at 90°C,
		CH ₃ COONH ₄ (3.2 mol/L 20%HNO ₃)	Shake for 1 h at room temperature
VI	Aluminosilicate bound fraction		Wet digestion

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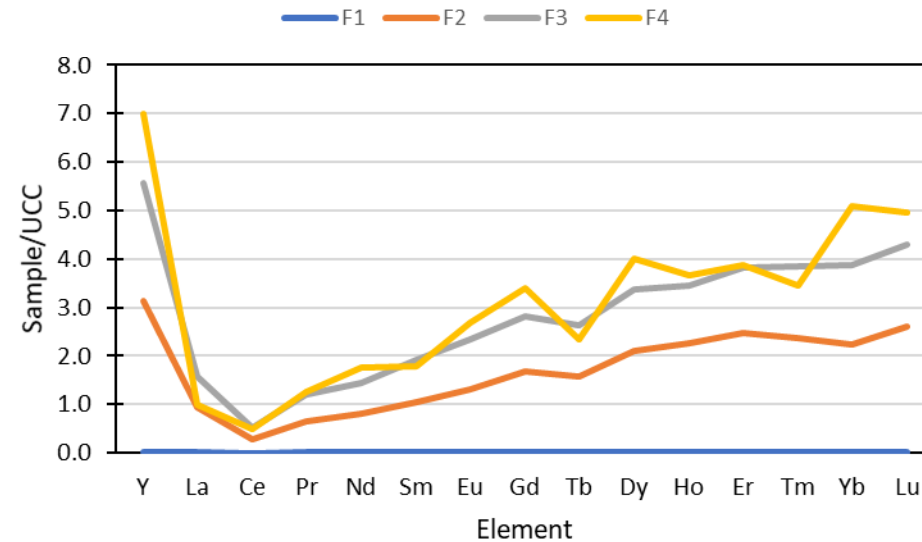
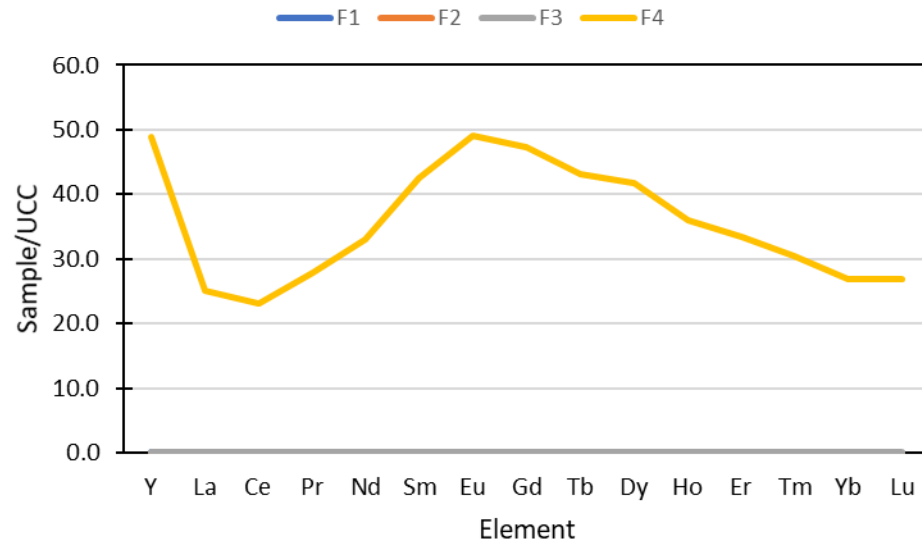
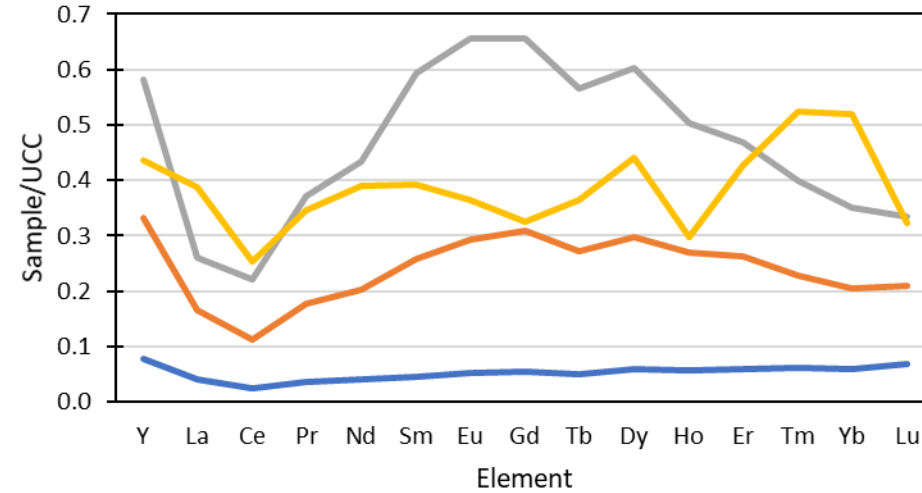
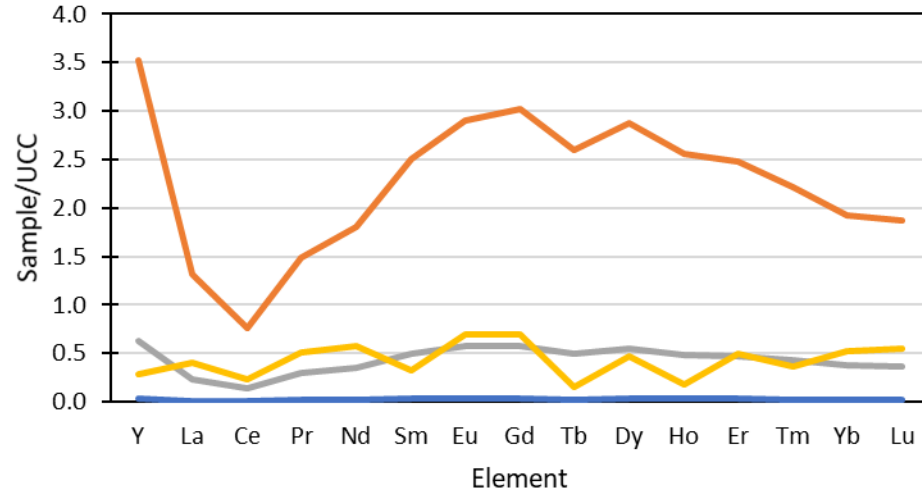
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REY speciation variations

F1	Water and acid soluble and exchangeable
F2	Sulfide phase
F3	Organic matter
F4	Silicates, crystalline phases, clays

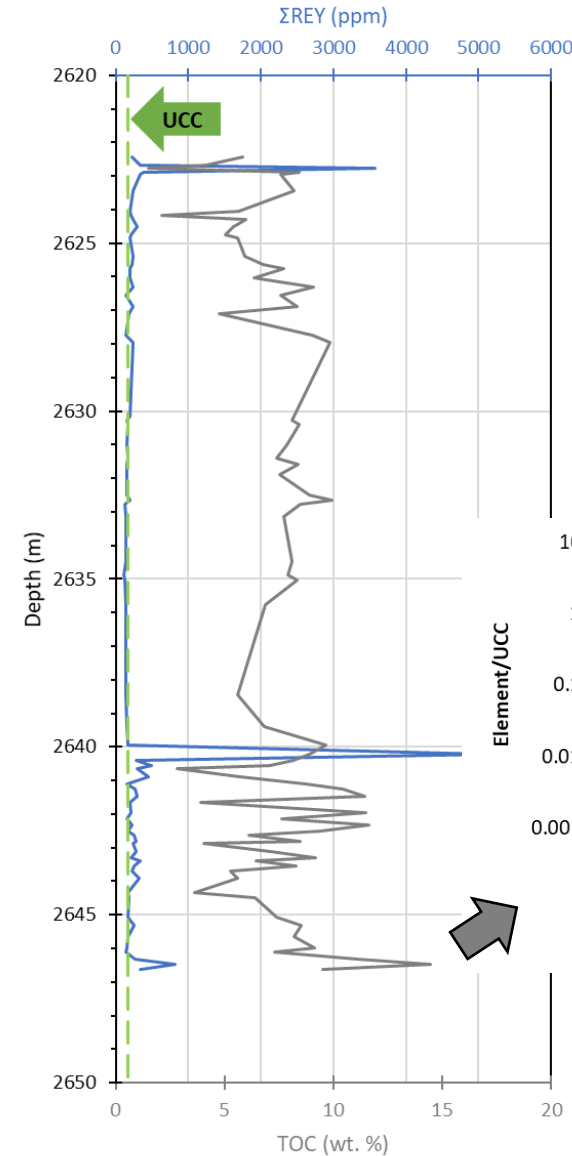
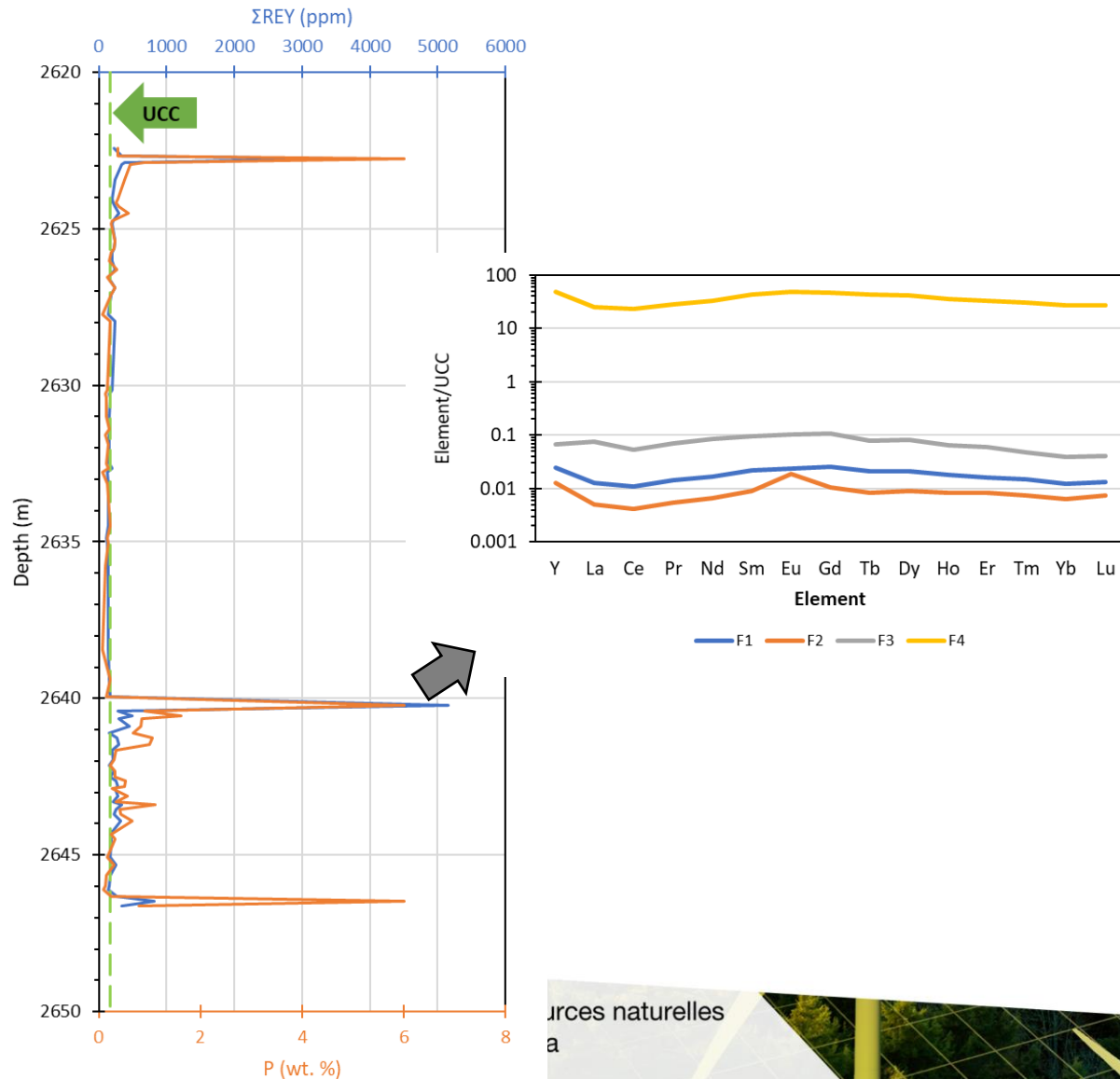
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REY speciation variations

16

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Summary

- The mean Σ REY of the major Canadian organic-rich source rocks are close or greater than mean UCC Σ REY, however, the range of variation throughout the unit is large.
- The highest Σ REY are associated with phosphatic intervals.
- REYs are mostly associated with silicate and clay phases, organic matter and sulfidic minerals are the second dominant hosts for REYs in black shales.
- Variation of REY speciation throughout the black shale intervals would be the major challenge for economic recovery of element.
- The initial results of this study suggest black shales can be considered a viable alternative source for critical REYs.



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